Alternating Spin and Orbital Dimerization in Strong-coupling Two-band Models

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We study a one-dimensional Hamiltonian consisting of coupled SU(2) spin and orbital degrees of freedom. Using the density matrix renormalization group, we calculate the phase-diagram and the ground state correlation functions for this model. We find that, in addition to the ferromagnetic and power-law antiferromagnetic phases for spin and orbital degrees of freedom, this model has a gapless line extending from the ferromagnetic phase to the Bethe ansatz solvable SU(4) critical point, and a gapped phase with doubly degenerate ground states which form alternating spin and orbital singlets. The spin-gap and the order parameters are evaluated and the relevance to several recently discovered spin-gap materials is discussed.

In recent years a remarkable number of new materials have been synthesized, which despite having magnetic ions have non-magnetic ground states, a finite correlation length and a gap in the spin-excitation spectrum. Among them, the spin-ladder forming Strontium Cuprates [1], the spin-Peierls systems Copper Germanates [2] and the periodically depleted Calcium Vanadates [3] have attracted the greatest attention. Here we discuss a novel spin-gap phase, which although mathematically closely related to the spin-ladder and spin-Peierls systems, is physically quite different. It arises in systems with spin and orbital degeneracy and requires coherence over neighboring atoms of both degrees of freedom. We also motivate such a spin-orbital model from a quantum-chemical analysis of recently discovered spin-gap materials $Na_2Ti_2Sb_2O$ [4] and $Na_2V_2O_5$ [5] and discuss the relevance of this new phase to them.

The two-band Hubbard model is well-known in context of magnetic insulators with Jahn-Teller ions [6]. The Hamiltonian is:

$$H = \sum t_{ij}^{\alpha\beta} c_{i\alpha\sigma}^{+} c_{j\beta\sigma} + \sum_{(\alpha\sigma)\neq(\beta\sigma')} U_{\alpha\beta} n_{i\alpha\sigma} n_{i\beta\sigma'}, \qquad (1)$$

where i, j are site indices, $\alpha, \beta = 1, 2$ the orbitals and σ, σ' the spin indices. Quarter filling of the bands amounts to one electron per atom. In the strong coupling limit this system is a Mott insulator, and the state of each ion can be characterized by a spin S_i and the orbital state can be mapped into a pseudospin $T = 1/2$ so that orbital one corresponds to $T^z = 1/2$ and orbital 2 to $T^z = -1/2$. Thus in the strong coupling limit, the effective spin-pseudospin Hamiltonian in one-dimension becomes [6]:

$$\mathcal{H} = J_1 \textstyle\sum_i \vec{S}_i \cdot \vec{S}_{i+1} + J_2 \sum_i (\vec{T}_i \cdot \vec{T}_{i+1} + A T_i^z T_{i+1}^z) + K \sum_i \vec{S}_i \cdot \vec{S}_{i+1} (\vec{T}_i \cdot \vec{T}_{i+1} + B T_i^z T_{i+1}^z) \qquad (2)$$

The simplest assumptions $t^{11} = t^{22} = t, t^{12} = 0$, together with a single U leads to

$$H = \sum_i \big(J_1 \vec{S}_i \cdot \vec{S}_{i+1} + J_2 \vec{T}_i \cdot \vec{T}_{i+1} + K (\vec{S}_i \cdot \vec{S}_{i+1})(\vec{T}_i \cdot \vec{T}_{i+1}) \big) \qquad (3)$$

with $J_1 = J_2 = K/4$. This special point has SU(4) symmetry. However, there are many ways in which one can find deviations from these parameters. For example, it was shown by Arovas and Auerbach [7] in the context of $C_{60} - TDAE$, that more than one $U_{\alpha\beta}$ leads to the Hamiltonian in Eq. 3 with the $SU(2) \times SU(2)$ symmetric parameter space reducing to $J_1 + J_2 = K/2$, but with J_1 not necessarily equal to J_2.

Here we study the ground states of this model with $SU(2) \times SU(2)$ symmetry with arbitrary J_1, J_2 and positive K. The calculated ground-state phase diagram is shown in Fig.1, where the Arovas-Auerbach line, $J_1 + J_2 = K/2$ is shown by the dotted line (which goes through point A). It is well known that the presence of orbital degrees of freedom can alter the nature of spin order, giving rise to both ferromagnetism and antiferromagnetism [6]. The ground states in phases I, II and III are known exactly. They are direct products of a spin and a pseudospin ground states. In phase I both spin and pseudospin degrees of freedom are fully polarized ferromagnets. In phase II the pseudospins are ferromagnetic whereas the spins are antiferromagnetic and their ground state is the Bethe Ansatz ground state of the spin-half antiferromagnetic chain. In phase III, spins and pseudospins are interchanged with respect to phase II. All these 3 phases are conventional magnetic phases appropriate for 1D, with gapless spin excitations. We will concentrate in the rest of the paper on the region IV, which we show has an excitation-gap, and the critical line AB, where gapless excitations exist. There are

two other points in the phase diagram, where the ground state is known exactly. The point A has SU(4) symmetry and is also Bethe-ansatz integrable [8]. It has gapless excitations and power-law correlations. The exact ground state for point C was recently obtained by Kolezhuk and Mikeska [9]. This ground state is doubly degenerate and there is a gap in the excitation spectrum.

To determine the properties of the region IV and the line AB, we turn to numerical methods. We use the density matrix renormalization group (DMRG) method [10] to calculate the ground state, the excitation gap and the spin and orbital correlation functions. The overall features of the method remain essentially the same for this problem as for the Heisenberg spin problems [11]. However, to treat the biquadratic term properly, and to take advantage of the enhanced symmetry, modifications are needed. It is known that the product of operators within the same block in the block density matrix eigenvector basis will be error prone, because the resolution of identity in the density-matrix basis is non-trivial [12]. This creates a difficulty in renormalizing the biquadratic term. To circumvent this difficulty, we have carried through any operator products required to construct the Hamiltonian matrix at every iteration. Besides, as the system posseses a global $SU(2) \times SU(2)$ symmetry, we define a single site with 4-states from the spin and orbital degrees of freedom and ensure that at every iteration both S^z_{tot} and T^z_{tot} are preserved as good quantum numbers.

We have used periodic boundary conditions throughout this study and have verified our results extensively. The ground state energy for point C (see Fig.1) is correct to numerical accuracy and the lowest excitation gap calculated to be 0.3756 in units of K compares with the variational estimate of 0.375 [9], with the DMRG cut-off, $m = 100$. At the SU(4) point (point A in Fig.1), the ground state energy is accurate with that obtained by the Bethe *ansatz* [8] to fourth significant decimal place and the excitation gap vanishes to numerical accuracy. We also verify the ground state energies and quantum numbers of phases I, II and III and obtain their phase boundaries by DMRG. In all our calculations described below, we have kept the cut-off m to be $120 < m < 150$. All the calculations are repeatedly checked by exact diagonalization results for small system sizes and we report here the results for system sizes upto $N \geq 30$. Note that, each site contains a spin and an orbital variable.

We have calculated the excited state energies in the subspace of $(S^{tot}_z, T^{tot}_z) = (1, 1)$ while the ground state remains in $(S^{tot}_z, T^{tot}_z) = (0, 0)$ subspace. For the line BA as well as for the whole of the incommensurate line(line AD in Fig.1), we have calculated the excitation gaps from the $N = 4n$ data. This is to avoid many-fold ground-state degeneracy for $N = 4n + 2$ [13]. Furthermore, to obtain these gaps in the thermodynamic limit, the calculated finite-size gaps, for the $N = 4n$ systems are fitted with a function of the form

$$\Delta(N) = \Delta + A/N + B/N^2 + C/N^3 + \ldots \qquad (4)$$

We find that the SU(4) critical point A is the endpoint of a critical line AB, where the point B, is a special point where several ground states, including the fully ferromagnetic spin and pseudospin ground states become exactly degenerate. At the SU(4) point, we have verified that the spin structure factor peaks at $q = \pi/2$ and the decay of the power-law real-space correlations are consistent with the 3/2-power [14]. Furthermore, all along the open interval AB, the structure factor peak remains at $q = \pi/2$. Also on this open interval, the ground state is a singlet and the spin and pseudospin gap remains zero. Numerically we find that the gap opens with an exponent of 1.5 ± 0.25 along the line AD close to the point A.

The point C is known to have degenerate ground states which can be written as a matrix-product consisting of alternating singlet bonds in both the spin and orbital variables [9]. There is a finite correlation length and the ground state spin structure factor peaks at $q = \pi$. Along the line AC above the SU(4) point A, the ground state remains doubly degenerate with a spin-gap (see Fig.1). This gap goes through a maximum at $J = J_1 = J_2 = (0.5 \pm 0.02)K$, while going from point C to point A where it vanishes to zero. Along this line, from point A to the point where the gap becomes maximum (point D in Fig.1), the spin as well as the pseudospin pair correlations are incommensurate. The peak in the structure factor moves from $q = \pi$ at D to $q = \pi/2$ at A.

Consider now the line which runs from point C to infinity with equal J_1/K and J_2/K values. All along this line, the spin-correlations stay peaked at $(q = \pi)$ and there is a finite spin gap. In the small K/J limit, the results are similar to those found for the ordinary spin ladder, where a gap opens for any finite interchain coupling. Our results are consistent with those of Nersesyan and Tsvelik [15] and Mostovoy [16] in that the gap is linear in K/J. In Fig.2, we plot the lowest excitation gap in units of $J = J_1 = J_2$, as a function of K/J.

Over the entire region IV, the ground state with $N = 4n$ is doubly degenerate. It is a spin and pseudospin singlet, with a finite excitation-gap. These results are in accordance with the Lieb-Schultz-Mattis theorem [17]. Furthermore, it has the same broken symmetry as the exactly solved point C. This is verified by calculating the square of the order parameter

$$\begin{aligned} Q^2(i-j) = \quad & < (S^z_i S^z_{i+1} - c)(S^z_j S^z_{j+1} - c) \\ & + (T^z_i T^z_{i+1} - c')(T^z_j T^z_{j+1} - c') > \end{aligned} \qquad (5)$$

for large $i - j$, where S^z_i and T^z_i are the z-component of spin and pseudospin operators respectively. c and c' are the average of two-particle correlations, i.e., $c = 1/N \sum_i < S^z_i S^z_{i+1} >$ and $c' = 1/N \sum_i < T^z_i T^z_{i+1} >$, N is the number of spin-orbital pairs. We find that Q^2 remains finite in this phase. In the context of spin degrees

of freedom, it is appropriate to mention here that the critical line (BA) and gapful phases of this model discussed above are similar to that of the Majumdar-Ghosh model for spin-1/2 chain with nearest and second neighbour exchanges [18].

We now turn to some recently synthesized spin-gap materials for which this model is relevant. The material $Na_2Ti_2Sb_2O$ was recently found to have a finite temperature phase transition at $T_c \approx 110K$ [4]. Below this temperature the uniform susceptibility drops sharply without any formation of magnetic order, and shows activated (spin-gap) behavior. In this material, the spin-half $Ti^{3+}(d^1)$ ions form a square lattice. Thus, this behavior is in marked contrast to the undoped Cuprates, which show antiferromagnetic order.

This material has inverse "K_2NiF_4" structure, consisting of layers of oxygen ions forming square-lattice, and Ti ions sitting in between them. The Sb ions are located above and below the centres of oxygen plaquettes as shown in Fig.3a. Each Ti ion is surrounded by four Sb ions and two oxygens, forming approximate octahedron. In this local tetragonal coordination, the triply degenerate t_{2g} levels are split into a doublet e_g and an a_1 levels. As the covalency of the Ti−Sb bond gives the main contribution to the crystal-field splitting, the e_g doublets should lie lower. Thus the ground state of Ti contains one d-electron in a doubly degenerate orbital, which choosing the O-Ti-O axis as the z-axis are the d_{xz} and the d_{yz} orbitals. These orbitals overlap through strong π-hybridization with the corresponding p_σ orbitals of Sb thus giving rise to two independent one dimensional structures extending along two mutually perpendicular axes of the crystal (see fig.3b). Thus to a first approximation this represents a quasi-1D quarter-filled 2-band system.

Magnetic properties of the material $Na_2Ti_2Sb_2O$, are qualitatively consistent with the gapped phase discussed here, although, more experiments are clearly needed to investigate the relevant atomic orbitals [19] and the nature of the low temperature phase of this system. It is also interesting to note that the isostructural material $Na_2Ti_2As_2O$ (where As replaces Sb) in many respect shows similar behavior above a certain temperature with a gradual reduction in magnetic susceptibility as the temperaure is lowered but also shows some evidence for ferromagnetism at very low temperature [20]. This could be expected from changing parameters in the spin-pseudospin models discussed above.

Another material that has recently gotten considerable attention is $Na_2V_2O_5$. This material is also a two-band quarter-filled quasi-1D Hubbard system [21]. In this case, the two orbitals arise from two chains of a ladder-like structure. Hence pseudospin ordering corresponds to charge ordering on different atoms [22–24]. It has been argued that in this material the spin-gap may be entirely due to charge ordering [24]. We note that at the SU(4) point, the spin and pseudospin correlations are peaked at $\pi/2$ and this is different from the period 1 and period 2 (ferro and antiferromagnetic) charge ordering scenarios, which have been discussed before. In the spin-gap phase discussed here, all atoms remain in an equivalent charge state. The question of whether such an alternating spin and orbital coherence between neighbors plays any role in this material deserves further attention.

In conclusion, we have used the density matrix renormalization group method to study the ground state, excitation-gap and correlation functions of an $SU(2) \times SU(2)$ spin-orbital model. We show that this model has a rich phase diagram. In addition to conventional ferromagnetic and antiferromagnetic phases in the spin and pseudospin variables, there is a gapless critical line which runs from the fully polarized ferromagnetic phase to the Bethe-ansatz solvable SU(4) critical point. We also find that over a wide parameter range this model has a broken symmetry gapped phase, where the system forms an alternating pattern of spin and orbital singlets. The relevance of this phase to various recently discovered spin-gap materials is discussed.

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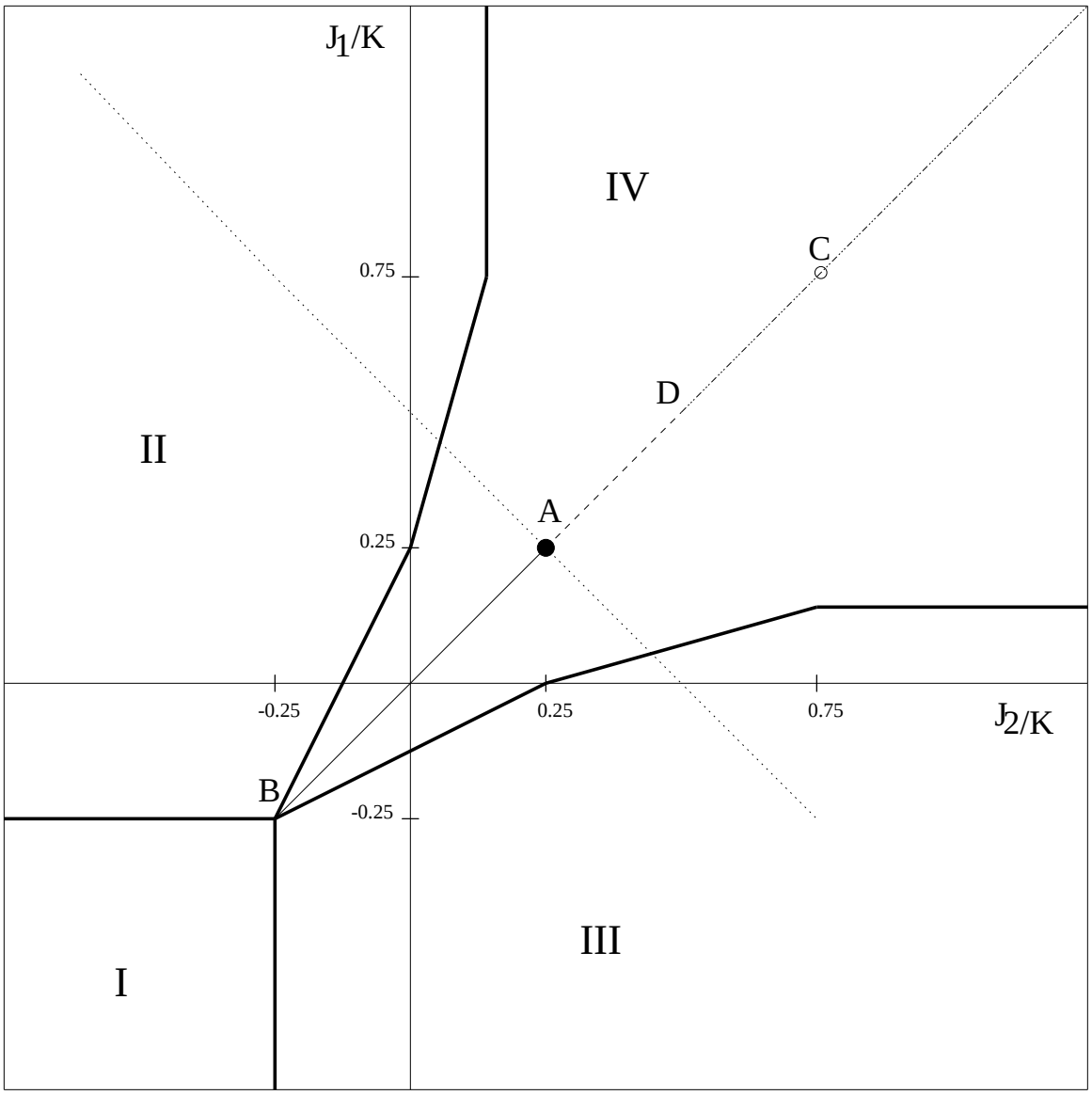
Figure Captions:

Fig.1: Phase Diagram for the model in Hamiltonian (3) in the J_1/K, J_2/K parameter space. Thick solid lines are 1st-order phase boundaries and BA is a critical line. See text for details.

Fig.2: Lowest excitation gap in units of J as a function of K/J for the line from point A to infinity through point D and C as in Fig.1.

Fig.3a: Structure of the material $Na_2Ti_2Sb_2O$.

Fig.3b: Cross-sectional view of the Titanium d_{xz} and d_{yz} orbitals, together with the p_z-orbitals of Sb in the X-Y plane. As shown, hoppings t^{11} (shaded-shaded)= t^{22} (unshaded-unshaded) = t and t^{12} (shaded-unshaded)= 0.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J2/K
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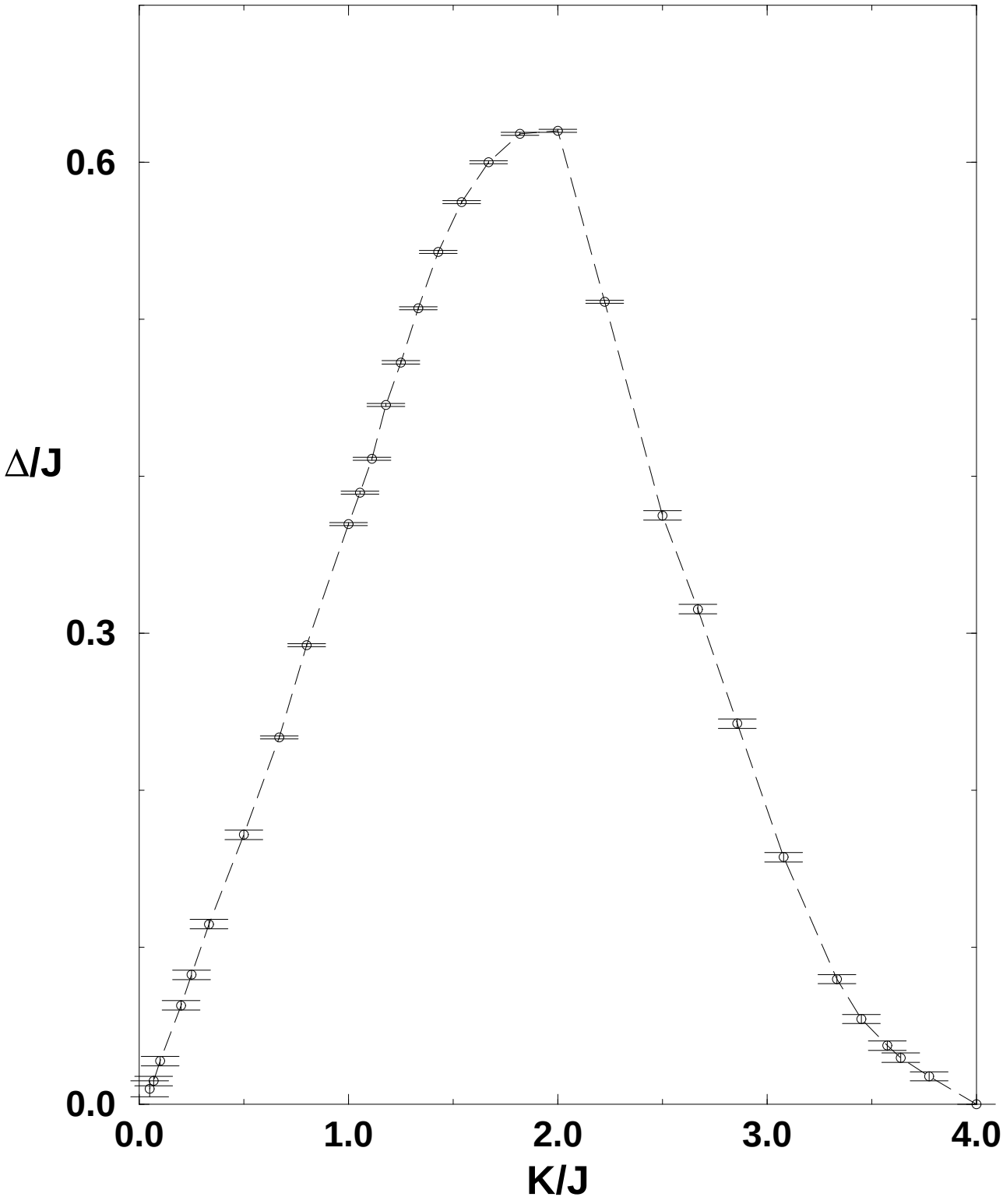
III
I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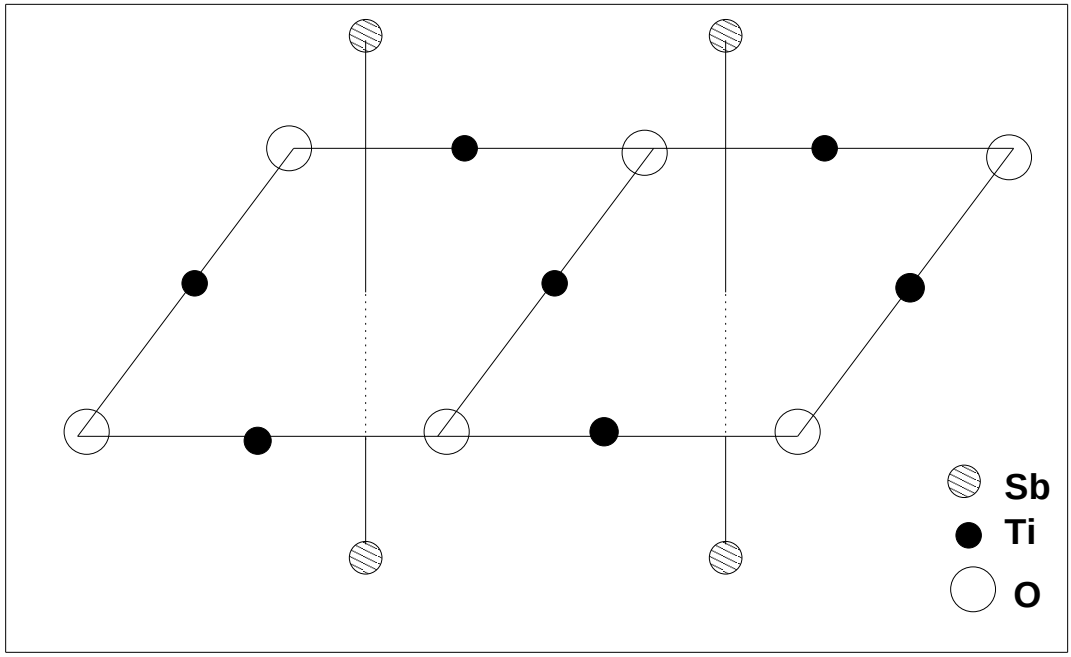
K/J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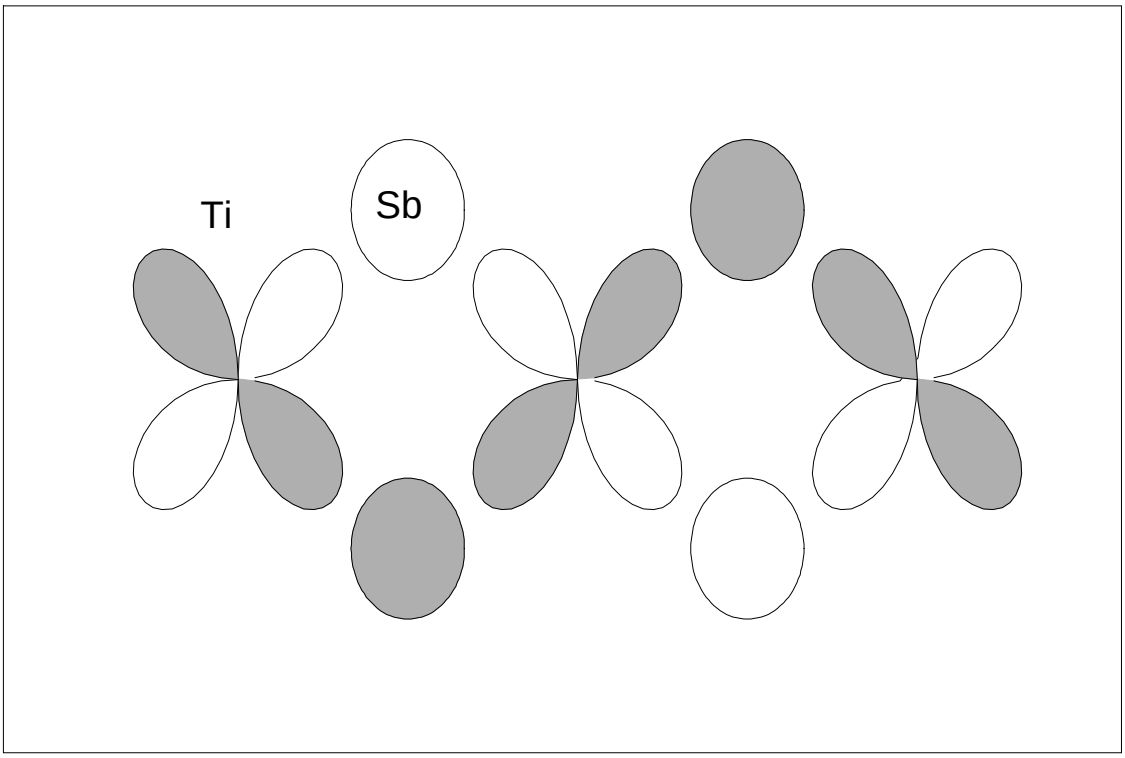
Ti
Sb